

Effect of root derived organic acids on the activation of nutrients in the rhizosphere soil

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Abstract: Four types of soils, including brown coniferous forest soil, dark brown soil, black soil, and black calcic soil, sampled from three different places in northeast China were used in this test. The functions of two root-derived organic acids and water were simulated and compared in the activation of mineral nutrients from the rhizosphere soil. The results showed that the organic acids could activate the nutrients and the activated degree of the nutrient elements highly depended on the amount and types of the organic acid excreted and on the physiochemical and biochemical properties of the soil tested. The activation effect of the citric acid was obviously higher than that of malic acid in extracting Fe, Mn, Cu, and Zn for all the tested soil types. However, the activation efficiencies of P, K, Ca, and Mg extracting by the citric acid were not much higher, sometimes even lower, than those by malic acid. The solution concentration of all elements increased with increase of amount of the citric acid added.

Key words: Organic acids; Nutrient; Activation; Rhizosphere

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Introduction

Root exudates may influence nutrient solubility and uptake indirectly through their effects on microbial activity, physiochemical properties of rhizosphere, and root growth patterns, and directly through acidification, chelation, precipitation and oxidation-reduction reactions (Uren and Reisenauer 1988). Soluble exudates of high molecular weight from maize root have been shown to form complexes with metal ions (Morel *et al.* 1986; Mench *et al.* 1987) and there is increasing evidence that soluble root exudates promote the solubility of the insoluble mineral nutrition (Godo and Reisenauer 1980; Uren 1984; Hoffland 1989b), probably because of the formation of soluble metal complexes (Merckx *et al.* 1986). The release of organic acids from the root has been suggested as a general mechanism for mobilizing metals from the soil's highly insoluble mineral phase. Of the root derived organic acids, citrate and malate are often released in the highest quantities in times of micronutrient deficiency (Jones and Darrah 1994). Both malate and citrate can form high-stability complexes with metal cations in the soil solution (Cline *et al.* 1987). However, the reaction of organic acids with metals in the soil depends not only on the complexation ability of the organic

acid, but also on solid phase sorption/desorption reaction, slower diffusion rates, microbial degradation, and hydrolysis of the organic acids by metal oxides. Therefore, the reaction of organic acid can be expected to be highly dependent on soil type. The purpose of this paper is to evaluate the role of organic acids in the activation of nutrients from the rhizosphere under various soil conditions.

Materials and methods

Four types of soils were used in this study. Black soil and black calcic soil were sampled from a broadleaf plantation in the Harbin Experimental Forest Farm of Northeast Forestry University. Samples of dark brown forest soil come from a mixed forest of conifers and broadleaf in the Changbai Mountain Research Station of Ecosystem of the Chinese Academy of Sciences, and sample of brown coniferous forest soil was collected from a conifer woodland in Daxing'anling Region of Heilongjiang Province. All the soil samples were collected from the upper 20-cm soil layer by removing the litter. Directly after collection from the field, the soil samples were air-dried and sieved to remove stones and dead fine roots. The general physical and chemical properties of the soils were analyzed by the standard methods issued by the State Standard Bureau (Table 1).

Firstly, the air-dried soil samples (1.5 g) were extracted with either 15-mL distilled water or 15 mL of a 500- $\mu\text{mol} \cdot \text{l}^{-1}$ citric acid or malic acid solution for one hour at room temperature on a rolling mixer, after then, the extracts were centrifuged and the supernatant were filtered. Finally, the solutions were analyzed for K, Ca, Mg, Fe, Mn, Cu and Zn with an atomic absorption spectrophotometer. By a

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color-contrasting method, we determined the phosphorous with a 721-spectrophotometer.

Phosphorous and other mineral elements released into the solutions with different concentrations of citric acid was assessed by extracting 1.0 g of black calcic soil with a

10-mL citric acid solution at concentrations ranging from 0-10 mmol·l⁻¹ for 30 min. Then the solutions were centrifuged and filtered. At last the solutions were analyzed for P and other mineral elements.

Table 1. Physiochemical characteristics of soil materials used

Soil type	pH	Org. (%)	Available nutrients							
			K /mg·kg ⁻¹	Ca /%	Mg /%	Fe /mg·kg ⁻¹	Mn /mg·kg ⁻¹	Cu /mg·kg ⁻¹	Zn /mg·kg ⁻¹	P /mg·kg ⁻¹
Brown coniferous forest soil	4.67	14.8	124.5	0.723	0.077	14.26	7.14	6.25	8.27	23.89
Dark brown soi	5.51	10.19	147.6	0.651	0.061	15.87	8.25	4.68	9.57	31.45
Black soil	5.67	16.9	141.8	0.687	0.067	12.54	6.36	4.97	8.46	27.30
Black calcic soil	6.38	7.43	103.5	1.104	0.082	9.62	7.65	5.33	5.94	16.69

Results and discussion

Effect of organic acids on activation of the elements from different soils

Although the extraction conditions were somewhat different from those existing in the rhizosphere soil, the extractions could provide a good reference of the possible role that those root-derived compounds may play in activating nutrients in the rhizosphere soil. Four contrasting soil samples were extracted with different organic acids and water. The concentrations of the nutrient elements released into the solutions were shown in Fig. 1. As expected, the activation efficiency of the organic acids playing to the elements is highly dependent on the soil types (See Table 2), for an example, the activation efficiency of P element extracting by citric acid was 0.0110, 0.0077, 0.0081, and 0.0221 for brown coniferous forest soil, dark brown soil, black soil, and black calcic soil, respectively.

In extracting Fe, Mn, Cu, and Zn the activation effect of the citric acid was much higher than that of malic acid in terms of the four soil types in our study (see Table 2 and Table 3). For brown coniferous forest soil, the activation efficiencies of Fe, Mn, Cu, and Zn extracting by citric acid were 134.5, 1.68, 10.89, and 3.84 times those of Fe, Mn,

Cu, and Zn extracting by malic acid, respectively. For black soil the activation efficiencies of Fe, Mn, Cu, and Zn by citric acid were 23.00, 3.04, 4.99, and 2.76 times those of Fe, Mn, Cu, and Zn by malic acid, respectively. However, The activation efficiencies of P, K, Ca, and Mg extracting by the citric acid were not much higher (sometimes even lower) than those extracted by the malic acid. For an example, the activation efficiencies of P and Mg extracting by citric acid were 0.0110 and 0.0530 separately, whereas those of P and Mn extracting by malic acid were 0.0148 and 0.0712 separately.

It can be concluded from the results presented above that the organic acids can activate the nutrients and the degree to which the nutrient elements are activated is highly dependent on the amount and type of the organic acids excreted and on the physiochemical and biochemical properties of the soil tested. Micronutrient deficiency symptoms, mainly resulting from the poor solubility of metal oxide and hydroxides in the soil solution, are often found in plants grown on calcareous soil or soils with high pH value. In these cases the organic acids released from the plant roots may play an direct important role in the activation of the insoluble nutrients, thus increasing the nutrient supply to the roots.

Table 2. Activation efficiency (μ mol activated / μ mol citric acid added) of the citric acid in activating the nutrient elements

Soils	P	K	Ca	Mg	Fe	Mn	Cu	Zn
Brown coniferous forest soil	0.0110	0.12	0.28	0.0530	0.1076	0.0442	0.1111	0.1221
Dark brown soi	0.0077	0.12	0.90	0.0514	0.0182	0.0822	0.1529	0.1455
Black soil	0.0081	-0.02	0.36	0.0086	0.0736	0.1097	0.0953	0.1305
Black calcic soil	0.0221	0.00	1.04	0.0548	0.0656	0.0931	0.0882	0.0814

Notes: Activation by water control has been subtracted. The same below.

Table 3. Activation efficiency (μ mol activated/ μ mol malic acid added) of the malic acid in activating the nutrient elements

Soils	P	K	Ca	Mg	Fe	Mn	Cu	Zn
Brown coniferous forest soil	0.0149	0.08	0.22	0.0712	0.0008	0.0263	0.0102	0.0318
Dark brown soi	0.0003	0.06	0.84	0.0480	0.0008	0.0170	0.0224	0.0710
Black soil	0.0011	0.00	0.30	-0.0018	0.0032	0.0361	0.0191	0.0472
Black calcic soil	0.0099	-0.02	0.66	0.0572	0.0182	0.0063	0.0309	0.0238

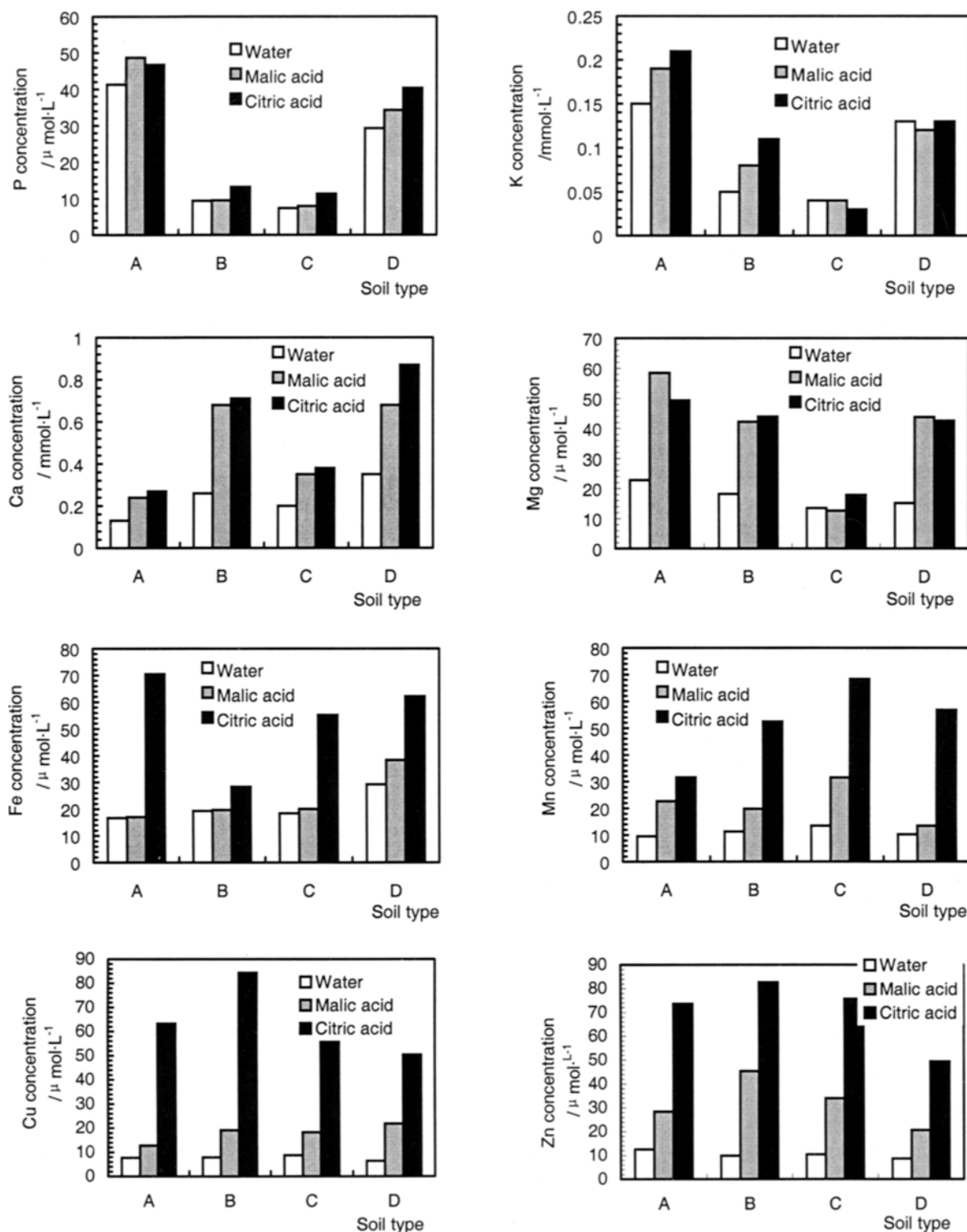


Fig. 1 Concentrations of P, K, Ca, Mg, Fe, Mn, Cu and Zn released into the solutions after the four types of soils were extracted by water, malic acid or citric acid ($500 \mu\text{mol}\cdot\text{L}^{-1}$)

A, B, C, D represent Brown coniferous forest soil, Dark brown soil, Black soil, and Black calic soil, respectively.

Effect of varied amount of citric acid on concentrations of elements released into solutions

The concentrations of P, K, Ca, Mg, Fe, Mn, Cu and Zn released into the solution of black calic soil as affected by different amount of citric acid added were shown in Fig. 2.

As expected, the amount of elements to be released into the solution increased with the increase of the amount of citric acid added. That is to say, the solution concentration of all elements increased with the increase of concentration of the citric acid. According to the amount of elements re-

leased into the solution with the same amount of citric acid added, the elements could be divided into three groups. The first group, including P, Fe, and Mn, released the smallest amount of elements into the solution, the second group including Mg, Cu, and Zn released a mediate amount of elements into the solution, and the third group, including K and Ca, released the largest amount of elements into the

solution. For example, when 20- μmol citric acid is added the released amounts of P, Fe, Mn, Mg, Cu, Zn, K, and Ca into the solution were 5.63, 5.81, 3.46, 9.16, 7.96, 8.72, 13.21, and 28.97 μmol , respectively. While a 50- μmol citric acid is added, the released amounts of P, Fe, Mn, Mg, Cu, Zn, K, and Ca into the solution were 12.73, 15.67, 7.38, 21.66, 17.20, 19.37, 45.20, and 59.20 μmol , respectively.

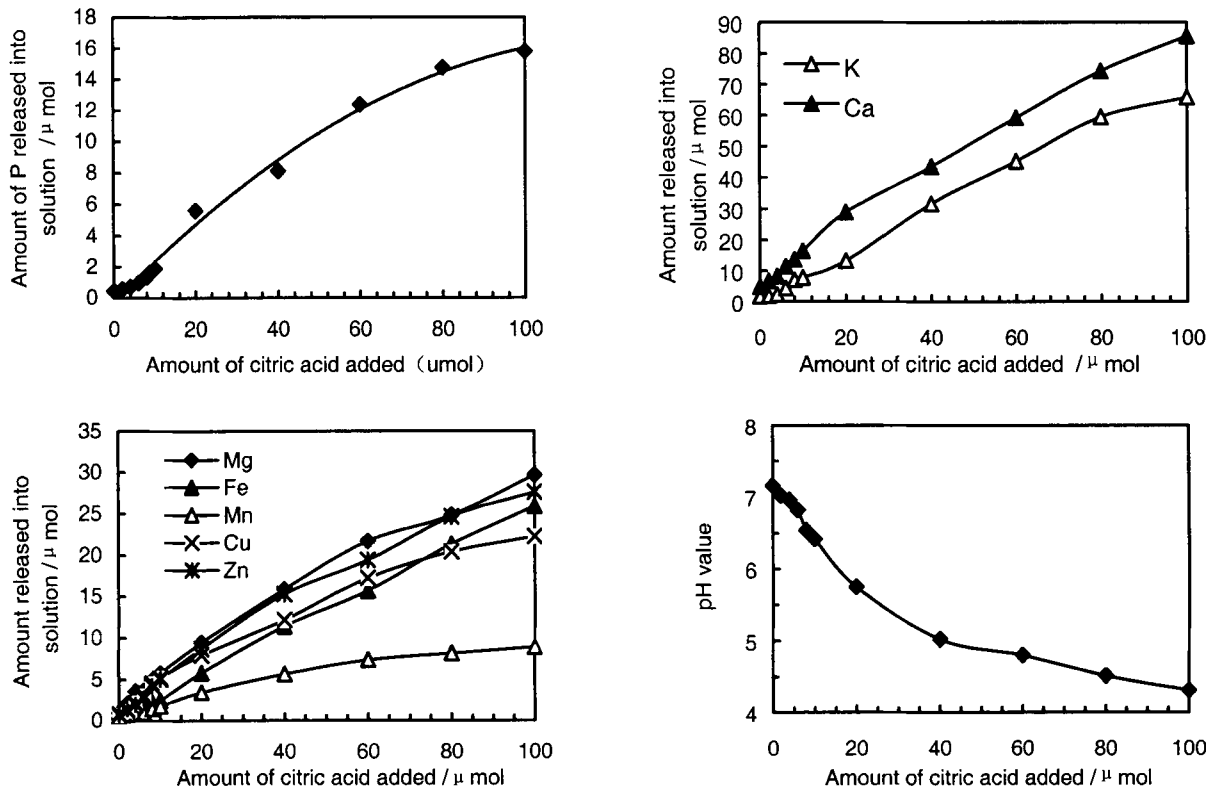


Fig. 2 Effect of different amount of citric acid on element release into the solutions

The H^+ concentration of the equilibrium solution also showed an increase with citric acid concentration rising due to the release of protons from citric acid during equilibrium. It's no doubt that both the citrate anions and the released protons were involved in dissolution, complexation, hydrolysis and exchange reaction with the soil's solution and solid phases. In order to distinguish the reactions between the proton and the citrate, extractions with HCl, NaCl and citrate should be carried out in the future study. Furthermore more studies should be carried out on evaluating the role of natural chelating compounds in the soil solutions in activation of the nutrients as most of the past research has focused on the synthetic chelors.

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